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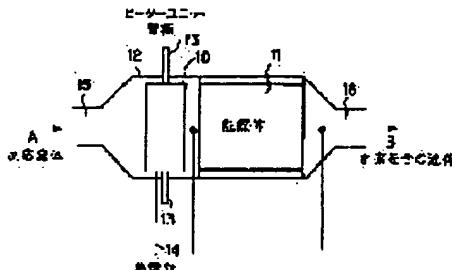
(72)Inventor : ABE FUMIO

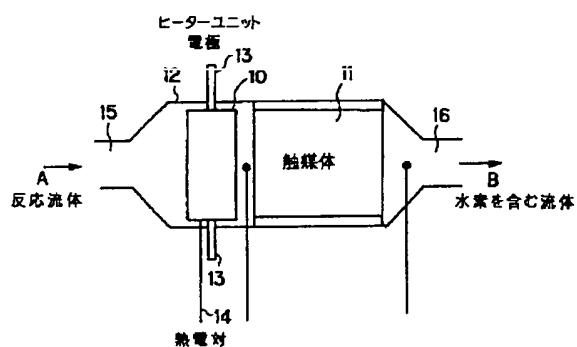
## (54) REFORMING REACTION DEVICE, CATALYTIC DEVICE, EXOTHERMIC CATALYTIC BODY USED FOR THE SAME AND OPERATION OF REFORMING REACTION DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a reforming reaction device capable of generating a high purity hydrogen for a fuel cell as industrial or on-vehicle use for a short time, a catalytic device, an exothermic catalytic body used for the same and the operating method.

SOLUTION: The reforming reaction device is formed by arranging the catalytic body 11 for generating hydrogen from a reaction fluid A containing an organic compound or carbon monoxide by the catalytic reaction and a heater unit 10 capable of generating heat by supplying current in a fluid flow passage 12. The exothermic catalytic body is constituted so as to contain one of a sintered compact, a metallic body and the combined body, at least a part of which has exothermic resistive property, and a combined body of a heat resistant body and/or a metallic body, which has no exothermic resistive property itself, and the catalyst capable of generating hydrogen from the reaction fluid containing the organic compound or carbon monoxide, to have porosity, into which the reaction fluid is diffused, and to enable to generate heat by passing current.



Drawing selection Representative drawing 

[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the operating method of the reforming reactor for hydrogen generating which can be suitably used as industrial use and an object for mount, catalyst equipment, generation of heat and the catalyst object that are used for them, and a reforming reactor.

[0002]

[Description of the Prior Art] In recent years, clean-ization in electric manufacture attracts attention, and the interest about a fuel cell is increasing. Generating efficiency of a fuel cell is high, and its yield of a carbon dioxide (CO<sub>2</sub>) is also low, and it has the advantage which, in addition, suppresses generating of harmful gas, such as a carbon monoxide (CO) and nitrogen oxides (NO<sub>x</sub>). Therefore, development for using a fuel cell for the electric organ and the object for mount of an on-site (On-site) mold recently is performed. In order to generate the electrical and electric equipment with a fuel cell, the hydrogen of a high grade is needed, and catalytic reaction generates hydrogen mainly by using alcohol, such as hydrocarbons, such as butane and a propane, and a methanol, CO, etc. as a start raw material.

[0003] Although the main reaction of hydrogen composition is a steam-reforming reaction (Steam Reforming) which occurs under existence of a steam and a catalyst, and it is dependent also on the matter of a start raw material, since it is the point how a catalyst is heated to the temperature of the request to homogeneity, and caulking will occur in it if reaction temperature falls in eye backlash which is generally endothermic reaction, and it leads to deactivation of a catalyst at it, as for this reaction, an industry top needs great concentration for the design of a reactor.

[0004] Moreover, although the above-mentioned steam-reforming reaction needed the comparatively big catalyst volume to throughput since the reaction rate was not quick like the combustion reaction, the technical field as which the pre-heating of a catalyst takes time amount since the operative temperature of a catalyst is high, and generating of hydrogen is promptly required of an on-site mold or mount had many problems.

[0005] In the conventional catalyst process, although the approach of carrying out heat tracing of the catalyst was generally used, in the case of fixed-bed flow system, it is difficult to tell heat to a catalyst-bed center section, and the complicated reaction process which heats the reactor of a multipipe type with heating media, such as a metal bath and a combustion gas, was needed with the

comparatively big coil.

[0006] Moreover, although the method of supplying a combustion gas (gaseous phase reaction and contact combustion) to the section of a reaction, and heating a catalyst by convective heat transfer as other conventional approaches is used, since CO<sub>2</sub> occurs by combustion while bringing about the fall of labile, in order to make a fluid flow rate increase, it cannot be said to be a desirable approach.

[0007] Moreover, in the generation gas obtained at the steam-reforming reaction, since it has a poisoning operation to Pt system electrode used for a fuel cell, CO which the purity of hydrogen generated like hydrogen highly [ in order to use for fuel cells ] raises the purity of hydrogen by CO water gas shift reaction (aquosity shift reaction) or alternative oxidation reaction of only CO. However, many technical problems occur about whether what we do into an operation condition with the pre-heating of these catalysts, and whether these reactions are advanced to stability.

[0008] As other reactions which generate hydrogen from a hydrocarbon etc., instead of a steam-reforming reaction, hydrogen and CO are generated and there is a method of obtaining hydrogen by the above-mentioned CO water gas shift reaction or CO alternative oxidation reaction by the partial oxidation reaction of a hydrocarbon. Although the 1st-step partial oxidation reaction is exothermic reaction and the problem about supply of heat is mitigated, generally reaction temperature is higher than a steam-reforming reaction, and there is no technique completed on the process about how the temperature of a catalyst is maintained too, and whether the hydrogen for the fuel cells of a high grade is generated an on-site mold and for mount for a short period of time. Furthermore, a decomposition reaction is mentioned as a reaction which generates hydrogen from a hydrocarbon etc. Although the decomposition reaction which generates hydrogen from a methanol specifically occurs, this reaction is endothermic reaction as well as a steam-reforming reaction, and has the same problem as the above.

[0009] Also in the industry which needs hydrogen in large quantities, for example, an ammonia synthesis reaction and a hydrogenation reaction, hydrogenation desulfurization, etc., reaction effectiveness is raised, it can operate by low energy, and starting of a reactor is shortened, and it can be said that there is room of amelioration plentifully in the point which does not discharge a unconverted gas.

[0010]

[Problem(s) to be Solved by the Invention] Therefore, the place which this invention is made in view of the technical problem of the above-mentioned conventional technique, and is made into the purpose is to offer the operating method of the reforming reactor which can generate the hydrogen for the fuel cells of a high grade in a short time, catalyst equipment, generation of heat and the catalyst object which are used for them, and a reforming reactor as industrial use or an object for mount.

[Means for Solving the Problem] According to this invention, the reforming reactor (1st invention) characterized by coming to arrange the catalyst object made to generate hydrogen by catalytic reaction from the reaction fluid containing an organic compound or a carbon monoxide and the heater unit in which energization generation of heat is possible in fluid passage is offered. Moreover, according to this invention, the reforming reactor (2nd invention) characterized by being the reforming reactor which comes to arrange the catalyst object made to generate

hydrogen in fluid passage, and these some catalyst objects [ at least ] being constituted from a reaction fluid containing an organic compound or a carbon monoxide by catalytic reaction possible [ generation of heat ] by energization is offered.

[0012] The sintered compact in which at least a part furthermore has an exoergic resistive characteristic by energization according to this invention, metallic objects, or these complex, Although there is no exoergic resistive characteristic in itself, or either of the complex with the heat-resistant matter, said sintered compact, and/or said metallic object, The catalyst which generates hydrogen by catalytic reaction is contained from the reaction fluid containing an organic compound or a carbon monoxide, and while having the porosity which makes a reaction fluid diffuse, generation of heat and the catalyst object (3rd invention) characterized by being constituted by energization possible [ generation of heat ] are offered.

[0013] The catalyst object which is made to generate hydrogen by catalytic reaction from the reaction fluid containing an organic compound or a carbon monoxide further again according to this invention, In the operating method of the reforming reactor which comes to arrange the heater unit in which energization generation of heat is possible in fluid passage The operating method of the reforming reactor characterized by making this heater unit generate heat by energization, and making hydrogen generate at the time of \*\*\*\* starting of this reactor (4th invention), And the catalyst object made to generate hydrogen by catalytic reaction from the reaction fluid containing an organic compound or a carbon monoxide is arranged in fluid passage. The operating method (5th invention) of the reforming reactor characterized by for these some catalyst objects [ at least ] making this catalyst object generate heat by energization, and making hydrogen generate in the operating method of the reforming reactor constituted by energization possible [ generation of heat ] at the time of \*\*\*\* starting of this reactor is offered.

[0014] Furthermore, according to this invention, the catalyst object made to generate hydrogen by catalytic reaction from the reaction fluid containing an organic compound or a carbon monoxide and the heater unit in which energization generation of heat is possible are set to the operating method of the reforming reactor which it comes to arrange in fluid passage. The operating method of the reforming reactor characterized by making this heater unit generate heat by energization, and generating hydrogen so that the reaction temperature of this catalyst object may be maintained at homogeneity (6th invention), And the catalyst object made to generate hydrogen by catalytic reaction from the reaction fluid containing an organic compound or a carbon monoxide is arranged in fluid passage. In the operating method of the reforming reactor with which these some catalyst objects [ at least ] are constituted by energization possible [ generation of heat ] The operating method (7th invention) of the reforming reactor characterized by making this catalyst object generate heat by energization, and generating hydrogen so that the reaction temperature of this catalyst object may be maintained at homogeneity is offered.

[0015] According to this invention, further again The heater unit in which energization generation of heat is possible, The catalyst equipment characterized by coming to arrange the catalyst object which causes endothermic reaction in fluid passage (8th invention), And the catalyst equipment (9th invention) characterized by coming to arrange the catalyst object containing the catalyst which some

catalyst objects [ at least ] are constituted by energization possible [ generation of heat ], and causes endothermic reaction in fluid passage is offered. Moreover, the sintered compact in which at least a part has an exoergic resistive characteristic by energization according to this invention, metalic objects, or these complex, Although there is no exoergic resistive characteristic in itself, or either of the complex with the heat-resistant matter, said sintered compact, and/or said metalic object, The catalyst which causes endothermic reaction is contained, and while having the porosity which makes a reaction fluid diffuse, generation of heat and the catalyst object (10th invention) characterized by being constituted by energization possible [ generation of heat ] are offered. Furthermore, according to this invention, the heater unit in which energization generation of heat is possible, and the catalyst object which causes endothermic reaction are set to the operating method of the catalyst equipment which it comes to arrange in fluid passage. The operating method of the catalyst equipment characterized by making this heater unit generate heat by energization (11th invention), And the catalyst object containing the catalyst which some catalyst objects [ at least ] are constituted by energization possible [ generation of heat ], and causes endothermic reaction is set to the operating method of the catalyst equipment which it comes to arrange in fluid passage. The operating method (12th invention) of the catalyst equipment characterized by making this catalyst object generate heat by energization is offered.

[0016]

[Embodiment of the Invention] According to this invention, optimum dose generating of the hydrogen of a high grade can be made to be able to carry out for a short period of time, and it can apply to it preferably as an on-site mold or a hydrogen generator for mount. Hereafter, although the gestalt of operation of this invention is explained, this invention is not limited to the gestalt of these operations.

[0017] In this invention, the reaction fluid which contains the organic compound or carbon monoxide (CO) which consists of alcohol, such as hydrocarbons, such as butane and a propane, and a methanol, as a start raw material for obtaining hydrogen is used. From a viewpoint of transportation of a bomb or a pipeline, although an alcoholic raw material like a gasoline or a methanol which can be carried with a liquid is desirable when a hydrocarbon considers the handling for mount preferably, it is not limited to these at all. CO is also a toxic gas and is not desirable as a start component.

[0018] The main reaction in the reforming reactor of this invention is a steam-reforming reaction which occurs under steam existence, and since CO of a by-product carries out poisoning of the electrode of a fuel cell in order to obtain H<sub>2</sub> of a high grade further, it reduces CO by CO water gas shift reaction or CO partial oxidation reaction. The example of a reaction using butane is shown below.

(1) C<sub>4</sub>H<sub>10</sub>+9H<sub>2</sub>O→9H<sub>2</sub>+4CO Steam-reforming reaction (2) CO+H<sub>2</sub>O→CO<sub>2</sub>+H<sub>2</sub> CO water gas shift reaction (3) CO+1/2O<sub>2</sub>→CO<sub>2</sub> CO alternative oxidation reaction [0019] As another reaction which obtains hydrogen, there is also the technique of using a partial oxidation reaction instead of a steam-reforming reaction.

(4) C<sub>4</sub>H<sub>10</sub>+2O<sub>2</sub>→4CO+5H<sub>2</sub> Partial oxidation reaction [0020] Following on a partial oxidation reaction, the reaction of the above (2) and (3) is usually advanced, and the purity of hydrogen is raised. Although the approach of acquiring the approach of obtaining hydrogen from a reaction (1) for hydrogen from a steam reforming process and a reaction (4) is called a partial oxidation method, this invention is

applicable to any approach. Although it is arbitrary about whether a steam reforming process is used or a partial oxidation method is used, for mount, the steam reforming process attracts attention by the partial oxidation method about alcohol, such as a methanol, in the gasoline. Generally, it is easy to obtain the hydrogen of a high grade at low temperature, and the steam reforming process is more efficient.

[0021] Moreover, there are the following two kinds as a reaction which generates hydrogen from a methanol.

(5)  $\text{CH}_3\text{OH} \rightarrow \text{CO} + \text{H}_2$  Decomposition reaction (endoergic)

(6)  $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}_2$  Steam-reforming reaction (endoergic)

[0022] Although the catalyst used for these reactions is mentioned later, a usually different catalyst is used and reaction temperature also differs. Generally the reaction of (1), (5), and (6) is endothermic reaction, and needs the temperature of 500 degrees C or more. (2) or (3) reaction -- exothermic reaction -- it is -- 300 degrees C or less -- it is made to go on at low temperature comparatively. The reaction of (4) is exothermic reaction and needs the reaction temperature of 500 degrees C or more too. in order to obtain the hydrogen of a high grade -- usually -- the above -- each catalyst is arranged for the reaction of (1 [(5), (6)]), (2), (3) or (4), (2), and (3) to a serial in fluid passage. [ or ] In addition, you may be a reforming reactor by (1) [(5), (6)] or the reaction of (4), and when using CO as a start raw material, (3) is made to react in the hydrogen concentration to need (2) or if needed. [ or ]

[0023] Hereafter, the operating method of the reforming reactor concerning this invention, catalyst equipment, generation of heat and the catalyst object that are used for them, and a reforming reactor is explained in detail. This application the 1st invention relates to the reforming reactor which comes to arrange the catalyst object made to generate hydrogen by catalytic reaction from the reaction fluid containing an organic compound or a carbon monoxide, and the heater unit which can be energized in fluid passage. One embodiment of this reforming reactor is shown in drawing 1.

[0024] In drawing 1, the heater unit 10 and the catalyst object 11 are arranged in the can (fluid passage) 12 of the quality of a metal, and constitute a reforming reactor. The heater unit 10 has an electrode 13 and the electrical and electric equipment is switched on from the external power which is not illustrated. Usually, the heater unit 10 is arranged at the upstream of the catalyst object 11. the sensor 14 for heater unit 10 control (a thermocouple etc. is included) is arranged at the back-wash side of the heater unit 10 or the heater unit 10. The reaction fluid A flows from an inlet port 15, and results in the outlet hole 16 through the heater unit 10 and the catalyst object 11. the fluid B containing the obtained hydrogen is conveyed to the fuel cell section arranged to the back-wash side of a reforming reactor.

[0025] although the cylinder which consists of a Nichrome presentation, and a tabular thing may be arranged all over fluid passage, in order to heat efficiently the catalyst object 11 arranged, for example to a back-wash side, the thing of a porous body, for example, the shape of cavernous tissue of 50% or more of hole density, a blanket-like thing, a filter-like thing, and the thing of the configuration of a honeycomb structure object (a tabular catalyst is also included) can apply the heater unit 10 suitably. Since especially the honeycomb structure object that has a linear through tube in the flow direction of the reaction fluid A

has small heat-conducting characteristic and pressure loss which are done to a reaction fluid, it is the most desirable.

[0026] The catalyst object 11 contains at least either of the catalyst components which has a catalysis about the above-mentioned steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, CO alternative oxidation reaction, etc. Among these, although CO alternative oxidation reaction is the purpose which reduces CO and it is not related to direct hydrogen composition, when you need high hydrogen concentration, it is important, and in order to incorporate in a reforming reactor, it includes in the catalyst object 11 in this invention.

[0027] Although the heating element itself is sufficient as the heater unit 10, it is more more desirable to contain either of the catalysts which has catalyses, such as a steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, and CO partial oxidation reaction, from the pre-heating property at the time of \*\*\*\* starting of the catalyst object 11 or a viewpoint of promotion of a reaction and temperature equalization of the catalyst object 11 at the time of steady operation. Although there is also a method of making a catalyst and a heating element intermingled as an approach of making a catalyst containing, the approach of carrying out covering support of the catalyst on the surface of a heating element can be used preferably. The heater unit which covered the catalyst on the honeycomb structure object which has a heat generation characteristic further on the spongy porous body which shows the above-mentioned heat generation characteristic from a viewpoint which can expect labile is the most desirable.

[0028] the sintered compact in which a heat generation characteristic is shown as an ingredient of the heater unit 10, i.e., barium titanate, (matter called a common name PTC and forward-like resistive characteristic), the carbide of SiC and MoSi<sub>2</sub> grade, the superconduction oxide of Y and Bi system, the oxygen ion conductor of perovskite or ZrO<sub>2</sub> grade in which the negative-like resistive characteristic is shown, other silicide, and a bora -- from the id, night RAID0, and the concept of a sintered compact, although it shifts, ion conductivity glass can be used.

Furthermore, as a metalic object in which an exoergic resistive characteristic is shown, although it does not have an exoergic resistive characteristic these metals and in itself [ the alloy presentation of the ferrite presentation of Fe-Cr-aluminum, nickel-Cr, Fe-aluminum Fe-Cr nickel-aluminum, etc., and ], the cermet which is the heat-resistant matter and which compounded the alumina etc. can be used.

[0029] The ingredient used for the above-mentioned heater unit is independent respectively, or it may be used, making it compound-ize. Moreover, compound-izing with a catalyst component is also possible. An important thing is that the property which generates heat by energization is shown, and it is not limited in ingredient. From the point of cost and manufacturability, the alloy presentation of Fe-Cr-aluminum, Fe-aluminum, Fe-Cr, etc. is desirable. These are already put in practical use as a catalytic converter for automobiles, and it excels also in thermal resistance and thermal shock resistance, and they have easily the advantage which can be created on a honeycomb structure object by the rolling method or the powder metallurgy method. As an example of the heater of a honeycomb structure object, what is shown in JP,3-295184,A ( drawing 2 ), and the thing ( drawing 3 ) shown in the Patent Publication Heisei No. 500911 [ three to ] official report are

mentioned.

[0030] The electrode 13 for energizing to the heater unit 10 is connected to the heater unit 10, and the electrical and electric equipment is supplied to it from an external power. It is possible to use the power source of a dc-battery, an AC dynamo, a capacitor (capacitor), etc., etc. in for mount. The heater unit 10 needs to adjust resistance according to injection power, an electrical potential difference, etc. Although these adjustment approaches are not limited, when the heater unit 10 is a honeycomb structure object, as shown in JP,3-295184,A and the Patent Publication Heisei No. 500911 [ three to ] official report, resistance can be adjusted by forming a slit and a gap.

[0031] The catalyst object 11 is used as a bead, a pellet, the shape of the shape of a grain, or a honeycomb, and a tabular configuration. Although a bead etc. is preferably used in respect of fluid mixing or heat conduction , since the reaction fluid in fluid passage is heated suitably and convective heat transfer is spread by heat mainly to the catalyst object 11 by combining with the heater unit 10 of this invention , it is desirable from the point of a pressure loss or a mechanical strength to use the honeycomb structure object which consists of the shape of a honeycomb or a tabular configuration . A honeycomb structure object means the structure which has the through tube (cel) substantially surrounded by the uniform septum, and also includes a tabular catalyst.

[0032] When using the catalyst object 11 as a configuration of a honeycomb structure object, covering support may be carried out and a catalyst component may be used for the honeycomb support which may honeycomb-ize catalyst component itself and consists of inactive ingredients, such as cordierite and a mullite.

[0033] The catalyst object 11 usually arranges the catalyst of anti-application [ oxidation / steam-reforming reaction, partial oxidation reaction and one reaction / of the decomposition reactions /, CO water gas shift reaction, and CO alternative ] to a serial. In the case of a honeycomb structure object, what classified each catalyst into one honeycomb structure object is sufficient as the catalyst object 11, but since reaction temperature differs, respectively, it is desirable to arrange two or more catalyst objects in a reforming reactor. It is because this gentleman can arrange arrangement of the heat exchanger for heat recovery, the introductory hole of auxiliary oxygen required for CO alternative oxidation reaction, etc.

[0034] As an array over the catalyst object 11 of the heater unit 10, as shown in drawing 4 , it is desirable to arrange for the maximum upstream of two or more catalyst objects 11 (catalyst object 11a [ 1st ], catalyst object 11b [ 2nd ], 3rd catalyst object 11c). Thereby, the pre-heating property of the catalyst object 11 whole improves. As another embodiment, as shown in drawing 5 , it is also possible to install heater unit 10b between [ other than heater unit 10a which divides the catalyst object 11 into plurality and is arranged for the maximum upstream ] 1st catalyst object 11a and 2nd catalyst object 11b. In this case, heater unit 10b will have the function which maintains an improvement of the pre-heating property of 2nd catalyst object 11b, and the temperature of 2nd catalyst object 11b at homogeneity. Moreover, it is also possible like drawing 6 to install the heater units 10b and 10c, respectively between 1st catalyst object 11a and 2nd catalyst object 11b and between 2nd catalyst object 11b and 3rd catalyst object 11c. Furthermore, as another embodiment, as shown in drawing 7 , it is also possible to arrange heater unit 10c to the last style side. in this case, it is because it may be necessary to

arrange the further catalyst object 11 to the back-wash side of that heater unit 10c if it is heater unit 10c which comes to support CO alternative oxidation catalyst. If the heater unit 10 contains the catalyst for a steam-reforming reaction or a partial oxidation reaction, CO water gas shift reaction, and CO partial oxidation reaction arbitrarily as for in [ how many ] the array sequence of the heater unit 10 and the catalyst object 11, and a reforming reactor it arranges like the above, combination like the heater unit 10, the catalyst object 11, and the heater unit 10 is also free.

[0035] The range of the typical reaction temperature for a steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, and CO partial oxidation reaction is 500 degrees C or more, 200-300 degrees C, and 100-200 degrees C, respectively. Therefore, catalyst object of a steam-reforming reaction, a partial oxidation reaction, or a decomposition reaction Between the catalyst objects of CO water gas shift reaction, since a temperature gradient arises, as shown in drawing 8 - drawing 9, it is desirable to arrange and carry out heat recovery of the heat exchanger 17 into fluid passage. The collected heat heats the reaction fluid A, or uses it for heating of the catalyst object 11.

[0036] The embodiment of drawing 8 is an example which has arranged the heat exchanger 17 between 1st catalyst object 11a and 2nd catalyst object 11b, and after heat exchange of the reaction fluid A is carried out by the heat exchanger 17 and it is heated with a carburetor 18, it is introduced in a can 12. In addition, it is also possible to carry out heat exchange of the reaction fluid A after heating with a carburetor. Here, although the class of heat exchanger 17 is not limited, a juxtaductal type heat exchanger, a tabular mold heat exchanger, etc. can be used. Although the embodiment of drawing 9 as well as drawing 8 is the example which has arranged the heat exchanger 17 between 1st catalyst object 11a and 2nd catalyst object 11b, as a fluid by which heat exchange is carried out, it may not be limited to a reaction fluid but it may be a heating medium. Although passing in the direction which needs the heat of the upstream is generally desirable as for the fluid after heat exchange, it may be poured to the downstream.

[0037] Next, this application the 2nd invention is explained. The catalyst object 20 made to generate hydrogen from the reaction fluid with which this application the 2nd invention contains an organic compound or a carbon monoxide is arranged in fluid passage, and some catalyst objects [ at least ] 20 are related with the reforming reactor constituted by energization possible [ generation of heat ]. The embodiment of this reforming reactor is shown in drawing 10 and drawing 11.

[0038] The catalyst object 20 is arranged in the can 21 of the quality of a metal, has the electrode 22 for energization in catalyst object 20 the very thing, and consists of a configuration that a part or the whole of the catalyst object 20 generates heat, by energization. In addition, drawing 10 is the configuration that the whole catalyst object 20 generates heat by energization, and drawing 11 shows the configuration in which some catalyst objects 20 generate heat by energization. Therefore, this application the 2nd invention has the function in which catalyst object 20 itself generates heat by energization, to the heater unit 10 and the catalyst object 11 being separately arranged in a can 12, as for the above-mentioned this application 1st invention, and essential effectiveness is made the same. In addition, the external power, the configuration of the sensor for temperature control and fluid passage, etc. are the same as the 1st invention.

[0039] Although it is the same as the heater unit 10 of the 1st invention, since

the configuration of the catalyst object 20 in the 2nd invention is held and energized in a can 21, its porous body of 50% or more of hole density is desirable, and it is the most desirable from the point of a heat-conducting characteristic or a pressure loss. [ of the thing of a honeycomb structure object ] Moreover, as shown in drawing 12 R> 2, the catalyst object 20 is put by making into a core material 23 the punching plate which consists of an ingredient in which energization generation of heat is possible, and a mesh-like metallic object, and, finally the structure which it comes to finish setting up to a honeycomb or a tabular module is also contained in the honeycomb structure object of this application.

[0040] Although it is most desirable to use as a porous base the ingredient in which the same generation of heat as the heater unit 10 of the 1st invention is possible, and to carry out covering support of the catalyst for a steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, and CO partial oxidation reaction on a base when using the porous catalyst object 20, it is not limited to this as well as the 1st invention.

[0041] Using as a base the honeycomb structure object which consists of an alloy presentation of Fe-Cr-aluminum, Fe-aluminum, Fe-Cr, etc. from the point of cost and manufacturability as most desirable example of the catalyst object 20, and carrying out covering support of the desired catalyst on this base is mentioned. In this case, it depends on the resistance adjusting method [ how the whole is generated heat partially ] in a catalyst object slack honeycomb structure object.

[0042] One suitable embodiment is shown below at drawing 13. Two or more slits 26 are formed near [ fluid inlet-port 25 ] the catalyst object 20 which consists of a honeycomb structure object, and a kind of current circuit is formed. one slit 27 is formed in the back-wash part of the catalyst object 20 which consists of a honeycomb structure object in the direction of the slit 26 of the fluid inlet port 25, and the mode which goes direct. By installing in a fluid inlet-port 25 close-attendants side, an electrode 28 serves as the structure where form the zigzag pass of a current along with the about 25 fluid inlet port slit 26 in this way, consequently only a fluid inlet-port 25 close-attendants side generates heat. Thus, a heat generation characteristic is controllable to a request by preparing a slit and a gap to make the catalyst object 20 partial generation of heat.

[0043] The technique as the above-mentioned in which the technique of making the whole catalyst object 20 generate heat is also the same can be used. Furthermore, by arranging two or more catalyst objects 20 which can generate heat by energization in fluid passage as a reforming reactor by this application the 2nd invention, and changing resistance of each catalyst object Adjust or so that the whole catalyst object may become uniform temperature A steam-reforming reaction, For every partial oxidation reaction or decomposition reaction, CO water gas shift reaction, and CO alternative oxidation anti-application The catalyst object which can be energized according to an individual is made to form, it can control by energization or the generating effectiveness of the hydrogen made into the purpose can be raised by the energization approach (time amount, power, timing adjustment) of a catalyst object in which further two or more energization is possible so that it may become desired temperature. In addition, this technique is applicable also in the heater unit in the 1st invention.

[0044] Even when it compares with the 1st invention and two or more catalyst objects which can be energized are used in the 2nd invention, as for each, it is

desirable that it is really an object. In addition, with this point Although heat conduction is also multiplied and it is easy to acquire high thermal-conversion effectiveness and uniform temperature distribution, it is desirable for it not to be necessary to heat the mass whole catalyst object superfluously, and to compound the 1st invention and invention of the 2nd in to use partial generation of heat \*\*\*\* if needed. In addition, as shown in drawing 14, when arranging the catalyst object 20 in which two or more energization is possible in a reforming reactor, energization control of each catalyst objects 20a, 20b, and 20c may be carried out independently, respectively, and it may connect with a serial or you may connect with connection and a pan with such combination at juxtaposition.

[0045] It is more desirable to heat the upstream, in order to raise the pre-heating nature of a catalyst object although the upstream, the downstream, and a core may be made to generate heat when making the catalyst object which can be energized generate heat partially. Moreover, how to attach distribution to radial is also considered. In the catalyst object of a steam-reforming reaction, in order that the core where the rate of flow of a reaction fluid is the quickest may bring about a bigger temperature fall by the reaction, a catalyst object with which a core generates heat from the periphery section is more desirable. This can say the same thing in the 1st invention also in the heater unit 10 arranged in the upstream (front) of the catalyst object 11 of a steam-reforming reaction, as shown in drawing 15.

[0046] Also in the 2nd invention, since the reaction temperature of a steam-reforming reaction, a partial oxidation reaction or a decomposition reaction, CO water gas shift reaction, and CO alternative oxidation reaction differs It is desirable to arrange two or more catalyst objects in a reforming reactor. A heat exchanger A steam-reforming reaction, it installs in the back-wash side of the catalyst object for a partial oxidation reaction or decomposition reactions, and heat recovery can be carried out and, ahead [ of CO alternative oxidation reaction / catalyst object ], an oxygen installation hole (installation of air is possible in practice) can be installed in heating a reaction fluid and a catalyst object \*\*\*\* if needed.

[0047] In the above, although the reforming reactor concerning this application the 1st and 2nd invention has been explained, the catalyst equipment which caught the above-mentioned invention from another viewpoint is explained below. That is, it is catalyst equipment (9th invention) which has arranged the catalyst object containing the catalyst which the catalyst equipment (8th invention) which has arranged the heater unit in which energization generation of heat is possible, and the catalyst object which causes endothermic reaction in fluid passage, and some catalyst objects [ at least ] are constituted by energization possible [ generation of heat ], and causes endothermic reaction in fluid passage. Thus, 8th and 9th invention is characterized by the point using the catalyst object as a means to give heat which at least a heater unit or a part can energization generate heat to the catalyst equipment which causes endothermic reaction, and the configuration of a heater unit and a catalyst object, a presentation, the quality of the material, and its array are the same as that of the 1st and 2nd above-mentioned invention. In addition, as an example of endothermic reaction, dehydrogenation besides a steam-reforming reaction which was described above, and a decomposition reaction can be mentioned.

[0048] Next, generation of heat and the catalyst object in this application the 3rd

invention are stated to a detail. In the 1st invention, although the matter in which the heat generation characteristic used as a heater unit 10 is shown was stated to the detail, also in the 3rd invention, the same matter is completely used as pyrogen. 3rd invention is characterized by having the porosity which the catalyst which generates hydrogen is contained [ porosity ] in this and makes it diffuse a reaction fluid. That is, although generation of heat and the catalyst object in the 3rd invention consist of a vesicular structure, 50 - 95% of range of hole density is desirable. If hole density brings about increase of pressure loss at less than 50% and hole density exceeds 95%, the fall of a porous body on the strength will be brought about.

[0049] The honeycomb structure object which has linear hole density to a reaction fluid in the porous body in generation of heat and a catalyst object is one of the desirable embodiments. A honeycomb structure object is formed with the gestalt containing the catalyst which generates the exoergic resistive-characteristic matter and hydrogen. Although it is as the term of the heater unit of the 1st invention having described in what kind of form pyrogen is included, it is most desirable to use the quality of a metal with a high heat-conduction property. The ferrite system metal in this case has highly desirable thermal resistance. For example, it is a Fe-Cr-aluminum system and, in the content of Cr, aluminum content can use 3 - 15% of the weight of a thing ten to 40% of the weight. Furthermore, it is desirable to add a small amount of additives, such as a lanthanum system element, and Si, Y, and to raise metaled thermal resistance. It is desirable to carry out covering support of the catalyst which generates hydrogen on the base of the honeycomb structure which consists of such quality of a metal.

[0050] Here, whether it is porosity or the base of honeycomb structure itself is nonvesicular like rolling foil metal, it is not cared about. Although reaction temperature is 900 degrees C or less, and exfoliation by the differential thermal expansion with the catalyst matter which the heat capacity of the base itself is [ to use a porous base ] smaller, and was covered on the base can be prevented when a thermal shock is not so large, either, it is fully usable also nonvesicular. As porosity of a base, 5 - 40% is desirable.

[0051] Moreover, an insulating material and a gap are made for the rolling (punching metal) foil which the hole opened as a desirable operation gestalt to intervene by rolling up from another viewpoint, the base in which a heat generation characteristic is shown is created, and the example which carries out covering support of the catalyst which generates hydrogen further is given. A reaction fluid diffuses also in radial the through tube of a fluid flow direction and the honeycomb structure object opened in parallel via the through tube in the foil while flowing. In this way, it is considered from radial heat transfer of a honeycomb structure object being performed that the catalyst of endothermic reaction is effective in equalization of temperature distribution especially like a steam-reforming reaction. Such a honeycomb structure object has a remarkable operation also in the usual honeycomb structure object which is not energized.

[0052] The hole equivalent diameter of the honeycomb structure object which constitutes generation of heat and a catalyst object has the desirable range of 0.5-10mm. this hole -- the case where an equivalent diameter is less than 0.5mm -- the rise of a pressure loss -- bringing -- on the other hand -- a hole -- the fall of labile will be brought about if an equivalent diameter exceeds 10mm. As the number of cels of a honeycomb structure object, the range of 4-1500 cel / square

inch is desirable, and it specifically decides suitably from a viewpoint of a pressure loss and labile.

[0053] As a catalyst which generates hydrogen from the reaction fluid containing an organic compound or a carbon monoxide, the component shown below can be used suitably. That is, at least one sort in the metallic element which belongs to a VB - VIII group, IB group, and an IIB group in the periodic table of a long period, and an oxide are included as a principal component.

[0054] As a metallic element effective in a steam-reforming reaction, a partial oxidation reaction, or a decomposition reaction, it is desirable to use a VIII group's metal as an indispensable component. as a desirable metallic element, it is nickel, Rh, Ru, Ir, Pd, Pt, Co, and Fe among them, and independent in these -- or it combines and uses. It is desirable to add VB group's V, Nb, a VIB group's Cr, Mn and W, and a VIIB group's Mn, Re, etc. as a co-catalyst for these metal components. Moreover, it is good as a carbon deposit inhibitor to also add alkaline earth metal. These metals are usually supported on a heat-resistant oxide. While raising the specific surface area of a catalyst and raising activity by this, the endurance over high reaction temperature is made to give.

[0055] As a heat-resistant oxide, aluminum 203, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and MgO or a zeolite, SAPO, ALPO, stratified compounds, and these multiple oxides can be used. That the specific surface area of whose is usually 5-300m<sup>2</sup>/g is used for these heat-resistant oxides. These heat-resistant oxides and the above-mentioned metal component are compounded by well-known technique, such as the chemical technique, such as dip coating, a coprecipitation method, and a sol gel process, and physical mixing. Also usually let specific surface area of the catalyst after composition be the range of 5-300m<sup>2</sup>/g. When the specific surface area of a catalyst is under 5m<sup>2</sup>/g, activity falls and 300m<sup>2</sup>/g is exceeded, the property change under an elevated temperature becomes remarkable, and it is inferior to endurance. In addition, about the range of this specific surface area, it corresponds also to the catalyst at large mentioned later.

[0056] As a heat-resistant oxide, an alumina (aluminum 203) is comparatively cheap, and in order to show a high specific surface area at the time of an elevated temperature, it can use preferably. Moreover, the multiple oxide of the spinel which made the alumina add a magnesia, and the magnesia singleness which is basic support in order to control a deposit of carbon or a magnesia can be used.

[0057] The rate of the catalyst metal added to a heat-resistant oxide has the desirable range of 1 - 30wt%. since activity is high in the case of the metal of a noble-metals system -- a maximum of 10 -- although it comes out enough even by addition of an about [ wt% ], in the case of metals of a base-metal system, such as nickel, it is desirable to consider as the range of 10 - 30wt%.

[0058] As a suitable catalyst for CO water gas shift reaction, although a VIII group's Fe, Co, IB group's Cu, an IIB group's Zn, etc. are often used, as for the metallic element specified by this application, the activity is shown not a little. The metal in which activity is shown at low temperature can secure thermal resistance by supporting these to heat-resistant oxides, such as the above-mentioned alumina, including Cu and Zn systems or both comparatively. As an addition to the heat-resistant oxide of the metal in this case, the range of 10 - 50wt% is desirable. In addition, when making it react at an elevated temperature comparatively, the spinel itself, such as Fe-Cr, can be used.

[0059]